CLAIMS

We claim:

 A method for reducing defects during the manufacture of semiconductor devices, the method comprising:

providing a substrate; and

contacting the substrate with a process solution comprising about 10 ppm to about 10,000 ppm of at least one surfactant having the formula (I) or (II):

$$R_3$$
 R_4
 R_3
 R_4
 R_5
 R_6
 R_7
 R_8
 R_9
 R_9

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wherein R_1 and R_4 are a straight or a branched alkyl chain having from 3 to 10 carbon atoms; R_2 and R_3 are either H or an alkyl chain having from 1 to 5 carbon atoms; and m, n, p, and q are numbers that range from 0 to 20.

- 2. The method of claim 1 wherein the process solution further comprises from about 10 to about 10,000 ppm of at least one dispersant.
- The method of claim 2 wherein the at least one dispersant comprises a nonionic compound.
- 4. The method of claim 2 wherein the at least one dispersant comprises an ioniccompound.
 - The method of claim 4 wherein the at least one dispersant comprises a surfactant.

- 6. The method of claim 1 wherein the value of (n + m) ranges from 0 to 30.
- 7. The method of claim 6 wherein the value of (n + m) ranges from 1.3 to 15.
- 8. The method of claim 1 wherein the value of (p + q) ranges from 0 to 30.
- 9. The method of claim 6 wherein the value of (p + q) ranges from 1 to 10.
- 5 10. The method of claim 1 wherein the contact angle is about 60° or less at 30 seconds.
 - 11. The method of claim 10 wherein the contact angle is about 50° or less at 30 seconds.
- 12. The method of claim 11 wherein the contact angle is about 40° or less at 30seconds.
 - 13. The method of claim 1 wherein the contacting step comprises a dynamic rinse.
 - 14. The method of claim 13 wherein the process solution exhibits a dynamic surface tension of about 45 dynes/cm² or less at 23°C and 1 bubble/second according to the maximum-bubble-pressure method.
 - 15. The method of claim 13 wherein the process solution exhibits substantially zero foam at a time greater than 60 seconds.
 - 16. A method for reducing defects during the manufacture of semiconductor devices, the method comprising:
- 20 providing a substrate; and

contacting the substrate with a process solution comprising about 10 ppm to about 10,000 ppm of at least one surfactant having the formula:

wherein R_1 and R_4 are a straight or a branched alkyl chain having from 3 to 10 carbon atoms; R_2 and R_3 are either H or an alkyl chain having from 1 to 5 carbon atoms; and m, n, p and q are numbers that range from 0 to 20.

17. A process solution, the solution comprising:

about 10 to about 10,000 ppm of at least one surfactant having the formula (I) or (II):

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wherein R_1 and R_4 are a straight or a branched alkyl chain having from 3 to 10 carbon atoms; R_2 and R_3 are either H or an alkyl chain having from 1 to 5 carbon atoms; and m, n, p, and q are numbers that range from 0 to 20.

- 18. The process solution of claim 17 wherein the process solution further comprises from about 10 to about 10,000 ppm of at least one dispersant.
- 19. The process solution of claim 18 wherein the at least one dispersant comprises a nonionic compound.

- 20. The process solution of claim 18 wherein the at least one dispersant comprises an ionic compound.
- 21. The process solution of claim 17 wherein the value of (n + m) ranges from 0 to 30.
- 5 22. The process solution of claim 21 wherein the value of (n + m) ranges from 1.3 to 15.
 - 23. The process solution of claim 17 wherein the value of (p + q) ranges from 0 to 30.
- The process solution of claim 23 wherein the value of (p + q) ranges from 1 to 10.
 - 25. The process solution of claim 17 further comprising a photoactive compound.
 - 26. The process solution of claim 17 further comprising a solvent.
 - 27. The process solution of claim 17 further comprising a polymer.
 - 28. The process solution of claim 17 further comprising a base.
- 15 29. The process solution of claim 17 further comprising an acid.
 - 30. A process solution, the solution comprising:about 10 to about 10,000 ppm of at least one surfactant having the formula:

wherein R_1 and R_4 are a straight or a branched alkyl chain having from 3 to 10 carbon atoms; R_2 and R_3 are either H or an alkyl chain having from 1 to 5 carbon atoms; and m, n, p, and q are numbers that range from 0 to 20.

31. A method for reducing the number of pattern collapse defects during the manufacture of semiconductor devices, the method comprising:

providing a substrate comprising a photoresist coating;

exposing the substrate to a radiation source to form a pattern on the photoresist coating;

applying a developer solution to the substrate to form a patterned photoresist coating;

optionally rinsing the substrate with deionized water; and contacting the substrate with a process solution comprising at least one solvent and 10 ppm to about 10,000 ppm of at least one surfactant having the formula (III), (IVa), (IVb), (V), (VI), (VII), or (VIII):

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$$R_1$$
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 R_5 (OCH₂CH₂)_tOH

 W

$$R_1$$
—NH NH— R_4 IVb

$$R_1$$
—NH N HN— R_4

$$X$$
 O
 R_1
 O
 R_4
 V

5 VIII

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wherein R_1 and R_4 are each independently a straight or a branched alkyl group having from 3 to 10 carbon atoms; R_2 and R_3 are each independently a hydrogen atom or an alkyl group having from 1 to 5 carbon atoms; R_5 is a straight or a branched alkyl group having from 1 to 10 carbon atoms; R_6 is a straight or a branched alkyl group having from 4 to 16 carbon atoms; R_7 , R_8 , and R_9 are each independently a straight or a branched alkyl group having from 1 to 6 carbon atoms; R_{10} is independently H or a group

represented by the formula

; R₁₁ is a straight, branched, or

cyclic alkyl group having from 4 to 22 carbon atoms; W is a hydrogen atom or an alkynyl group; X and Y are each independently a hydrogen atom or a hydroxyl group; Z is a halide atom, a hydroxyl group, an acetate group, or a carboxylate group; m, n, p, and q are each independently a number that ranges from 0 to 20; r and s are each independently 2 or 3; t is a number that ranges from 0 to 2; j is a number that ranges from 1 to 5; and x is a number that ranges from 1 to 6.

- 32. The method of claim 31 wherein the contacting step comprises a dynamic rinse.
- 33. The method of claim 31 wherein the contacting step comprises a static rinse.
- 34. The method of claim 31 wherein the surface of the substrate in the contacting step is wet with the developer solution.

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- 35. The method of claim 31 wherein the surface of the substrate in the contacting step is wet with the deionized water rinse.
- 36. The method of claim 31 wherein the solvent comprises an aqueous solvent.
- 37. The method of claim 36 wherein the solvent comprises a non-aqueous solvent wherein the non-aqueous solvent is miscible in the aqueous solvent.
- 38. The method of claim 31 wherein the process stream is formed by injecting 10 to 10,000 ppm of the at least one surfactant into the solvent.
- 39. The method of claim 31 wherein the process stream is formed by applying 10 to 10,000 ppm of the at least one surfactant onto the surface of the substrate and applying the solvent to the substrate surface.
- 40. The method of claim 31 wherein the process stream is formed by passing the solvent through a cartridge comprising the at least one surfactant.
- 41. The method of claim 31 wherein a time of the contacting step ranges from 1 to 200 seconds.
- 20 42. The method of claim 40 wherein the time of the contacting step ranges from 1 to 150 seconds.
 - 43. The method of claim 41 wherein the time of the contacting step ranges from 1 to 40 seconds.
- The method of claim 31 wherein an at least one temperature of the contacting step ranges from 10 to 100°C.

45. A method for avoiding a collapse of a developed pattern on the surface of a plurality of substrates, the method comprising:

providing a first substrate comprising a photoresist pattern developed upon the surface;

preparing a process solution comprising from 10 ppm to about 10,000 of at least one surfactant having the formula (I), (II), (IVa), (IVb), (V), (VI), (VII), or (VIII):

$$R_3$$
 R_4
 R_3
 R_4
 R_2
 R_1
 R_1

R₁

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$$R_5$$
 (OCH₂CH₂)_tOF

$$R_1$$
—NH N HN— R_4

$$R_1$$
—NH NH— R_4

$$X$$
 O
 R_1
 O
 R_4

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wherein R_1 and R_4 are each independently a straight or a branched alkyl group having from 3 to 10 carbon atoms; R_2 and R_3 are each independently a hydrogen atom or an alkyl group having from 1 to 5 carbon atoms; R_5 is a straight or a branched alkyl group having from 1 to 10 carbon atoms; R_6 is a straight or a branched alkyl group having from 4 to 16 carbon atoms; R_7 , R_8 , and R_9 are each independently a straight or a branched alkyl group having from 1 to 6 carbon atoms; R_{10} is independently a H atom or a group represented by the formula

having from 4 to 22 carbon atoms; W is a hydrogen atom or an alkynyl group; X and Y are each independently a hydrogen atom or a hydroxyl group; Z is a halide atom, a hydroxyl group, an acetate group, or a carboxylate group; m, n, p, and q are each independently a number that ranges from 0 to 20; r and s are each independently 2 or 3; t is a number that ranges from 0 to 2; j is a number that ranges from 1 to 5; and x is a number that ranges from 1 to 6;

contacting the first substrate with the process solution;

determining a surface tension and a contact angle of the process solution on the first substrate;

multiplying the surface tension by the cosine of the contact angle to provide the adhesion tension value of the process solution;

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providing the plurality of substrates wherein each substrate within the plurality comprises a photoresist pattern developed upon the surface; and contacting the plurality of substrates with the process solution if the adhesion tension value of the process solution is 30 or below.

- 46. The process of claim 45 wherein the preparing, the first contacting, the determining, and the multiplying steps are repeated until the adhesion tension value is 30 or below.
 - 47. The process of claim 45 wherein the surface of the plurality of substrates in the second contacting step is wet with a deionized water rinse.
- 15 48. The process of claim 45 wherein the surface of the plurality of substrates is wet with a developer solution.
 - 49. A process rinse solution to reduce pattern collapse defects on the surface of a substrate that has been patterned and developed, the solution comprising at least one carrier medium selected from the group consisting of an aqueous solvent or a non-aqueous solvent and at least one surfactant selected from the group of surfactants having the formula (III), (IVa), (IVb), (V), (VI), (VII), or (VIII):

$$R_5$$
 (OCH₂CH₂)₁OH (CH₂)r (CH₂)s R_1 NH N HN— R_2

III IVa $X \longrightarrow Q$ $X \longrightarrow Q$ X

VIII

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wherein R_1 and R_4 are each independently a straight or a branched alkyl group having from 3 to 10 carbon atoms; R_2 and R_3 are each independently a hydrogen atom or an alkyl group having from 1 to 5 carbon atoms; R_5 is a straight or a branched alkyl group having from 1 to 10 carbon atoms; R_6 is a straight or a branched alkyl group having from 4 to 16 carbon atoms; R_7 , R_8 , and R_9 are each independently a straight or a branched alkyl group having from 1 to 6 carbon atoms; R_{10} is a hydrogen atom or a group represented by the formula

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group having from 4 to 22 carbon atoms; W is a hydrogen atom or an alkynyl group; X and Y are each independently a hydrogen atom or a hydroxyl group; Z is a halide atom, a hydroxyl group, an acetate group, or a carboxylate group; m and n are each independently a number that ranges from 0 to 20; r and s are each independently 2 or 3; t is a number that ranges from 0 to 2; j is a number that ranges from 1 to 5; and x is a number that ranges from 1 to 6.

- 50. The process solution of claim 49 wherein the at least one carrier medium comprises an aqueous solvent.
- The process solution of claim 50 wherein the at least one carrier medium comprises a non-aqueous solvent wherein the non-aqueous solvent is miscible in the aqueous solvent.
 - 52. The process solution of claim 49 wherein the at least one carrier medium is an aqueous solvent and the at least one surfactant is a surfactant having the following formula (III):

$$R_1$$
 R_5
 $OCH_2CH_2)_tOH$
 W
 III

wherein R_1 is a straight or a branched alkyl group having from 3 to 10 carbon atoms; R_5 is a straight or a branched alkyl group having from 1 to 10 carbon atoms; W is a hydrogen atom or an alkynyl group; and t is a number that ranges from 0 to 2.

53. The process solution of claim 49 wherein the at least one carrier medium is an aqueous solvent and the at least one surfactant is a surfactant having the following formula (IVa):

$$R_1$$
—NH N HN— R_2

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wherein R_1 and R_4 are each independently a straight or a branched alkyl group having from 3 to 10 carbon atoms and r and s are each independently 2 or 3.

54. The process solution of claim 49 wherein the at least one carrier medium is an aqueous solvent and the at least one surfactant is a surfactant having the following formula (IVb):

wherein R_1 and R_4 are each independently a straight or a branched alkyl group having from 3 to 10 carbon atoms and r is 2 or 3.

55. The process solution of claim 49 wherein the at least one carrier medium is an aqueous solvent and the at least one surfactant is a surfactant having the following formula (V):

$$X$$
 O
 R_1
 O
 R_4

wherein R₁ and R₄ are each independently a straight or branched alkyl group having from 3 to 10 carbon atoms and X and Y are each independently a hydrogen atom or a hydroxyl group.

56. The process solution of claim 49 wherein the at least one carrier medium is an aqueous solvent and the at least one surfactant is a surfactant having the following formula (VI):

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wherein R_6 is a straight or a branched alkyl group having from 4 to 16 carbon atoms; R_7 , R_8 , and R_9 are each independently a straight or a branched alkyl group having from 1 to 6 carbon atoms; and Z is a halide atom, a hydroxyl group, an acetate group, or a carboxylate group.

15 57. The process solution of claim 49 wherein the at least one carrier medium is an aqueous solvent and the at least one surfactant is a surfactant having the

following formula (VII):

$$R_2$$
 (OCH₂CH₂)mOH
 $(CH_2)_j$
 R_3 (OCH₂CH₂)nOH
 R_4

wherein R_1 and R_4 are each independently a straight or branched alkyl group having from 3 to 10 carbon atoms; R_2 and R_3 are each independently a hydrogen atom or an alkyl group having from 1 to 5 carbon atoms; m and n are each independently a number that ranges from 0 to 20; and j is a number that ranges from 1 to 5.

58. The process solution of claim 49 wherein the at least one carrier medium is an aqueous solvent and the at least one surfactant is a surfactant having the following formula (VIII):

$$R_{10}$$
 $N = (CH_2)_r - N = (CH_2)_s - N = 0$ R_{10} R_{10} R_{10}

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wherein R₁₀ is a hydrogen atom or a group represented by the formula

O—
$$R_{11}$$
 ; R_{11} is independently a straight, branched, or cyclic

alkyl group having from 4 to 22 carbon atoms; r and s are each independently 2 or 3; and x is a number that ranges from 1 to 6.